

United States Patent Application for

COMPOSITES OF INORGANIC LUMINOPHORES STABILIZED IN POLYMER HOSTS

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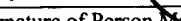
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COMPOSITES OF INORGANIC LUMINOPHORES STABILIZED IN POLYMER HOSTS

This invention relates to composites, and in particular to a class of stabilized luminescent polymer(plastic) composites for use in two and three dimensional luminescent displays, and the invention is a Continuation-In-Part of U.S. application 09/448,657 filed November 24,1999, which has the same assignee as the subject invention, and a common inventor with the subject invention, which claims the benefit of U.S. Provisional application 60/109,837 filed November 25, 1998, by the same assignee as the subject invention, and the invention was funded in part under U.S. Army Contract DAAD199910220.

BACKGROUND AND PRIOR ART

The doping of heavy metal luminophores in commercially available optical grade plastics, such as poly (methyl methacrylate) or polystyrene, generally results in the aggregation of the metal salt. This aggregation leads to excessive light scattering, weakening of the plastic's mechanical strength, and an inhomogenous composite that would be unsuitable for optical or display applications.

Using a monochromatic display has been well known. However, monochromatic displays do not offer adequate color type detail such as reds, greens and blue colors.

Displays using liquid crystals have been proposed for generating color displays. See for example, U.S. Patents 5,359,345 and 5,724,062 to Hunter. However, these patents require arranging individual pixels in rows and corresponding columns, column 4, lines 36-39. The devices described can be expensive and complicated to manufacture, and can have narrow angular view ranges with low brightness.

Additional display systems have been proposed with similar problems to those described above. See for example, U.S. Patents 4,791,415 to Takahashi; 4,871,231 to Garcia, Jr.; 5,184,114 to Brown; 5,192,946 to Thompson et al.; and 5,317,348 to Knize.

Several patents have been proposed for panel displays using two-frequency upconversion fluorescence. See for example, U.S. Patents 5,684,621; 5,764,403; 5,914,807; 5,943,160; and

5,956,172 all to Downing. The Downing '403 patent appears to be the most relevant to the subject invention. Downing '403 is primarily concerned with embodiments where the use of different layers for red, green and blue emitters, abstract, Fig. 6, and briefly describes some mixing of only crystal type materials in a single display media. However, for the single display media, Downing '403 uses nanometer sized particles, column 4, lines 33+, column 9, lines 42-45, which would inherently be difficult to form, handle and disperse in a display medium.

Other known patents such as U.S. Patents 5,003,179 to Pollack; 5,051,278 to Paz-Pujalt; 5,154,962 to Mertens et al.; 5,245,623 to McFarlane; 5,622,807 to Cutler; 5,846,684 to Paz-Pujalt et al. also fail to overcome the problems with the other patents described above.

SUMMARY OF THE INVENTION

The primary objective of this invention is to provide an inexpensive display medium for two and three dimensional displays.

The secondary objective of this invention is to provide a transparent polymer(plastic) containing particles doped with rare ions for use as display medium for two and three dimensional displays.

The third objective of this invention is to provide homogeneously dispersed compositions in a polymer composition without cracking or delamination

The fourth objective of this invention is to provide a display medium for the up conversion of near infrared light to the visible for two and three dimensional displays.

The fifth objective of this invention is to provide an inexpensive display medium that is versatile for various optical system applications.

The sixth objective of this invention is to provide homogeneously dispersed compositions in a polymer composition that can be used as plastic optical fiber amplifiers.

The invention can be used with up conversion displays with specific applications for two and three dimensional displays such as those described in parent patent applications 09/448,657

filed November 24, 1999, by the same assignee as the subject invention and of which is incorporated by reference.

A novel polymer composition for display mediums according to the subject invention can include a co-polymer composite of an alkyl material and a phosphonate material, and luminescent metal ions dispersed in the composite, wherein the composition can be used for displays. The alkyl material can be an alkyl acrylate, and alkyl methacrylate. The phosphate material can be dialkyl vinylbenzylphosphonate, alkyl vinylbenzylphosphonic acid monoester, and vinylbenzylphosphonic acid .

The composition can have a molar ratio of approximately 20% to approximately 95% acrylate material, and approximately 80 %to approximately 5% phosphate material.

The luminescent metal ions can include rare earth compounds, and NaYF₄:ErYb. The composite can be phosphorylated polymethyl methacrylate(p-PPMA).

The luminescent metal ions can include rare earth ions co-doped with Yb³⁺ in fluoride and orthophosphate crystalline hosts. The doping ion can be Tm, Er, Ho, Nd, Pr, and Ce. The crystalline hosts can include NaYF₄, KYF, YLF, and LuPO₄.

A method of making a polymer composition is also disclosed and includes steps of forming a co-polymer from an alkyl material and a phosphonate material, and dispersing luminescent metal ions in the co-polymer without cracking and delaminating of the co-polymer.

Further objects and advantages of this invention will be apparent from the following detailed description of a presently preferred embodiment which is illustrated schematically in the accompanying drawings.

BRIEF DESCRIPTION OF THE FIGURES

Fig. 1 shows the stabilization of the dispersed heavy element luminophores being accomplished through complexation with the phosphoryl moieties.

DETAILED DESCRIPTION OF THE INVENTION

Before explaining the disclosed embodiment of the present invention in detail it is to be understood that the invention is not limited in its application to the details of the particular arrangement shown since the invention is capable of other embodiments. Also, the terminology used herein is for the purpose of description and not of limitation.

As previously described, the subject invention can be used with up conversion displays with specific applications for two and three dimensional displays such as those described in parent patent applications 09/448,657 filed November 24, 1999, by the same assignee as the subject invention and of which is incorporated by reference.

The subject invention is for a class of luminescent polymer(plastic) composites for use in two and three dimensional luminescent displays. The polymer composite can contain phosphonate or phosphonic acid functional groups that complex the heavy metal luminophore, leading to a homogeneous dispersion of the luminophore. The polymer or plastic host facilitates formation of a stabilized luminescent, thermoplastic polymer composite that can be cast as conformal thin films, molded in sheets, conformal geometries, and the like. The conformal thin films can be plastic films that can be formed over any surface geometry, having thickness of approximately 1mm to approximately 200 mm, and be formed from processes such as but not limited to spin coating, and the like. The molded Sheets can be Sheets of various thickness formed by melt processing, and the like, having thickness of approximately 0.1 mm to approximately 25 mm, and be formed from processes such as but not limited to melt processing, compression molding, and the like. The conformal geometries would include any geometry, planar or non planar.

The polymeric composites are prepared from commercially available materials and are low cost, and can include any acrylate material, any methacrylate, material, any styrene material, and the like. The low cost factor of these materials, can be approximately \$20/kg.

Fig. 1 shows the stabilization of the dispersed heavy element luminophores being accomplished through complexation with the phosphoryl moieties.

Table 1 is a list of various crystals and co dopants and central wavelengths of the bands of visible emission detected following excitation with a diode laser source operating at 968 nm.

Table 1.

Doping ion $\text{Yb}^{3+} +$	Crystal host	Peak emission wavelength (nm)		
		blue	green	Red
Tm^{3+}	NaYF_4	450, 475		647, 698
	KYF	481		652
	YLF	483		648
	LuPO_4	475		649, 704
Er^{3+}	NaYF_4	411	540	660
	KYF		550	654, 670
	YLF		541, 549	654, 668
	LuPO_4		526, 550	657, 667
Ho^{3+}	NaYF_4		540	648
	KYF		544	658

Table 1: Visible emission of Tm, Er and Ho after Yb excitation in different hosts

In Table 1, Yb^{3+} refers to ytterbium, Tm^{3+} refers to thulium, Er^{3+} refers to erbium, Ho^{3+} refers to holmium, NaYF_4 refers to crystal sodium yttrium fluoride, and the superscript 3+ refers to the triply ionized state of the atom. Referring again to Table 1, KYF is short for KYF_4 and refers to crystal, potassium yttrium fluoride. YLF is short for YLiF_4 and refers to the crystal, yttrium lithium fluoride. LuPO_4 refers to the crystal, lutetium orthophosphate.

The crystals and dopants listed in Table 1 are illustrative of a few of the combinations that can be used. Other lanthanide(rare earth) atoms in the 3+ state can also be used as dopants.

For example, Nd^{3+} , Pr^{3+} , Ce^{3+} and the like, can also be used. There can be other oxide and fluoride crystals that can serve as host crystals. Transition metal dopants such as but not limited to Cr^{3+} , Ti^{3+} and the like, can serve as dopants in these host crystals as well. Additionally, other crystals and activators that can be used for this invention can include those listed from pages 171 to page 311 listed in Laser Crystals by Alexander Kaminski, (Springer Verlag, New York) SBN 0-387-09576-4, 1981. These crystals and their activators can include but are not limited to the following described activators and crystal combinations.

Activator Pr^{3+} and crystals can include: LiYF_4 , $\text{Ca}(\text{NbO}_3)_2$, CaWO_4 , and SrMoO_4 .

Activator Nd^{3+} and crystals can include: LiYF_4 , LiYO_2 , LiNbO_3 , $\text{LiNbP}_4\text{O}_{12}$, CaF_2 , SrF_2 , BaF_2 , LaF_3 , CeF_3 , NaF , NaCaYF_6 , NaCaCeF_6 , $\text{NaNdP}_4\text{O}_{12}$, YF_3 , CaYF , SrYF , CeO_2 , GdF_3 , YF_3 , LuF_3 , CdF_2 , $\text{KY}(\text{MoO}_4)_2$, $\text{KY}(\text{WO}_4)_2$, $\text{KNdP}_4\text{O}_{12}$, $\text{KGd}(\text{WO}_4)_2$, CaMg_2Y_2 , CaAl_4O_7 , $\text{CaAl}_{12}\text{O}_{19}$, CaSc_2O_4 , $\text{Ca}_3(\text{VO}_4)_2$, $\text{Ca}(\text{NbO}_3)_2$, CaMoO_4 , CaWO_4 , SrAl_2O_7 , $\text{SrAl}_{12}\text{O}_{19}$, SrMoO_4 , SrWO_4 , Y_2O_3 ,
5 YAlO_3 , $\text{Y}_3\text{Al}_5\text{O}_{12}$, Y_2SiO_5 , YP_5O_{14} , $\text{Y}_3\text{Sc}_2\text{Al}_3\text{O}_{12}$, $\text{Y}_3\text{Sc}_2\text{Ga}_3\text{O}_{12}$, YVO_4 , $\text{Y}_3\text{Ga}_5\text{O}_{12}$, $(\text{Y}, \text{Lu})_3\text{Al}_5\text{O}_{12}$, $\text{Ba}_{0.25}\text{Mg}_{2.75}\text{Y}_2$, LaBe_2O_5 , La_2O_3 , LaAlO_3 , $\text{LaP}_5\text{O}_{14}$, LaNbO_4 , $\text{CeP}_5\text{O}_{14}$, $\text{NdAl}_3(\text{BO}_3)_4$, $\text{NdP}_5\text{O}_{14}$, Gd_2O_3 , GdAlO_3 , $\text{GdP}_5\text{O}_{14}$, GdScO_3 , $\text{Gd}_3\text{Sc}_2\text{Al}_3\text{O}_{12}$, $\text{Gd}_3\text{Sc}_2\text{Ga}_3\text{O}_{12}$, $\text{Gd}_3\text{Ga}_5\text{O}_{12}$, $\text{Gd}_2(\text{MoO}_4)_3$, LuAlO_3 , $\text{Lu}_3\text{Ga}_5\text{O}_{12}$, PbMoO_4 , $\text{Bi}_4\text{Si}_3\text{O}_{12}$, $\text{Bi}_4\text{Ge}_3\text{O}_{12}$, $\text{LiLa}(\text{MoO}_4)_2$, $\text{Li}(\text{Nd}, \text{La})\text{P}_4\text{O}_{12}$, $\text{Li}(\text{Nd}, \text{Gd})\text{P}_4\text{O}_{12}$, $\text{LiGd}(\text{MoO}_4)_2$, $\text{NaLa}(\text{MoO}_4)_2$, $\text{NaLa}(\text{WO}_4)_2$, $\text{Na}_3\text{Nd}(\text{PO}_4)_2$, $\text{Na}_5\text{Nd}(\text{WO}_4)_2$,
10 $\text{Na}_3\text{Gd}(\text{WO}_4)_2$, $\text{Na}(\text{Nd}, \text{Gd})$, $\text{K}(\text{MoO}_4)_2$, $\text{K}_3\text{Nd}(\text{PO}_4)_2$, $\text{K}_3(\text{Nd}, \text{La})$, $\text{K}_3\text{Nd}(\text{MoO}_4)_4$, $\text{K}_5\text{Bi}(\text{MoO}_4)_4$, $\text{CaY}_4(\text{SiO}_4)_3\text{O}$, $\text{Ca}_{0.25}\text{Ba}_{0.75}$, $\text{CaLa}_4(\text{SiO}_4)_3\text{O}$, $\text{CaLa}(\text{PO}_4)_3\text{O}$, $\text{CaGd}_4(\text{SiO}_4)_3\text{O}$, YScO_3 , $\text{Y}_2\text{Ti}_2\text{O}_7$, $\text{ZrO}_2\text{-Y}_2\text{O}_3$, $\text{Ba}_2\text{MgGe}_2\text{O}_7$, $\text{Ba}_2\text{ZnGe}_2\text{O}_7$, $(\text{Nd}, \text{Sc})\text{P}_5\text{O}_{14}$, $(\text{Nd}, \text{In})\text{P}_5\text{O}_{14}$, $(\text{Nd}, \text{La})\text{P}_5\text{O}_{14}$, $(\text{Nd}, \text{Gd})\text{Al}_3$, LuScO_3 , $\text{HfO}_2\text{-Y}_2\text{O}_3$, $\text{Bi}_4(\text{Si}, \text{Ge})_3\text{O}_{12}$, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, $\text{Sr}_5(\text{PO}_4)_3\text{F}$, and $\text{La}_2\text{O}_2\text{S}$, CeCl_3 , $\text{Pb}_5(\text{PO}_4)_3\text{F}$.

Activator Ho^{3+} and crystals can include: LiYF_4 , $\text{Li}(\text{Y}, \text{Er})\text{F}_4$, LiNbO_3 , CaF_2 , LiHoF_4 , BaY_2F_8 , $\text{Ba}(\text{Y}, \text{Er})_2\text{F}_8$, HoF_3 , CaF_2 , YF_3 , ErF_3 , NaCaErF_6 , $\text{K}(\text{Y}, \text{Er})(\text{WO}_4)_2$, $\text{KGd}(\text{WO}_4)_2$, $\text{Ca}(\text{NbO}_3)_2$, CaMoO_4 , CaWO_4 , YAlO_3 , $\text{Y}_3\text{Al}_5\text{O}_{12}$, Y_2SiO_5 , YVO_4 , $\text{Y}_3\text{Fe}_5\text{O}_{12}$, $\text{Y}_3\text{Ga}_5\text{O}_{12}$, $(\text{Y}, \text{Er})\text{Al}_3$, $(\text{Y}, \text{Er})_3\text{Al}_5\text{O}_{12}$, LaNbO_4 , GdAlO_3 , $\text{Ho}_3\text{Al}_5\text{O}_{12}$, $\text{Ho}_3\text{Sc}_2\text{Al}_3\text{O}_{12}$, $\text{Ho}_3\text{Ga}_5\text{O}_{12}$, Er_2O_3 , ErAlO_3 , Er_2SiO_5 , $\text{Er}_3\text{Sc}_2\text{Al}_3\text{O}_{12}$, ErVO_4 , $(\text{Er}, \text{Tm}, \text{Yb})_3$, $(\text{Er}, \text{Lu})\text{AlO}_3$, $\text{Yb}_3\text{Al}_5\text{O}_{12}$, LuAlO_3 , $\text{Lu}_3\text{Al}_5\text{O}_{12}$,
20 $\text{NaLa}(\text{MoO}_4)_2$, $\text{CaY}_4(\text{SiO}_4)_3\text{O}$, $\text{SrY}_4(\text{SiO}_4)_3\text{O}$, $\text{SrLa}_4(\text{SiO}_4)_3\text{O}$, $\text{ZrO}_2\text{-Er}_2\text{O}_3$, $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$, and $\text{Ca}_5(\text{PO}_4)_3\text{F}$.

Activator Er^{3+} and crystals can include: LiYF_4 , LiErF_4 , CaF_2 , BaY_2F_8 , $\text{Ba}(\text{Y}, \text{Er})_2\text{F}_8$, LaF_3 , YF_3 , ErF_3 , $\text{K}(\text{Y}, \text{Er})(\text{WO}_4)_2$, $\text{KGd}(\text{WO}_4)_2$, CaAl_4O_7 , $\text{Ca}(\text{NbO}_3)_2$, CaWO_4 , YAlO_3 , $\text{Y}_3\text{Al}_5\text{O}_{12}$, $(\text{Y}, \text{Er})_3\text{Al}_5\text{O}_{12}$, GdAlO_3 , $\text{Er}_3\text{Al}_5\text{O}_{12}$, $(\text{Er}, \text{Lu})_3\text{Al}_5\text{O}_{12}$, $\text{Yb}_3\text{Al}_5\text{O}_{12}$, LuAlO_3 , and $\text{Lu}_3\text{Al}_5\text{O}_{12}$.

25 Activator Ni^{2+} and crystals can include: MgF_2 , MnF_2 , and MgO . Activator V^{2+} and crystals can include: MgF_2 . Activator Co^{2+} and crystals can include: MgF_2 , KMgF_2 , and ZnF_2 .
Activator Yb^{3+} and crystals can include: CaF_2 , Nd^{3+} , $\text{Y}_3\text{Al}_5\text{O}_{12}$, $\text{Y}_3\text{Ga}_5\text{O}_{12}$, $(\text{Y}, \text{Yb})_3\text{Al}_5\text{O}_{12}$,

Gd₃Sc₂Al₃O₁₂, Gd₃Ga₅O₁₂, (Yb, Lu)₃Al₅O₁₂, Lu₃Al₅O₁₂, Lu₃Sc₂Al₃O₁₂, and Lu₃Ga₅O₁₂. Activator Sm²⁺ and crystals can include: CaF₂, SrF₂. Activator Dy²⁺ and crystals can include: CaF₂, SrF₂. Activator Dy³⁺ and crystals can include: Ba(Y,Er)₂F₈. Activator Tm²⁺ and crystals can include: CaF₂.

5 Activator Tm³⁺ and crystals can include: CaF₂, SrF₂, ErF₃, NaCaErF₆, LiNbO₃, Ca(NbO₃)₂, CaMoO₄, CaWO₄, YAlO₃, Y₃Al₅O₁₂, YVO₄, (Y, Er)Al₃, (Y, Er)₃Al₅O₁₂, GdAlO₃, Er₂O₃, ErAlO₃, Er₃Al₅O₁₂, (Er, Yb)₃Al₅O₁₂, (Er, Lu)AlO₃, Lu₃Al₅O₁₂, and ZrO₂-Er₂O₃.

Activator U³⁺ and crystals can include: CaF₂, SrF₂, and BaF₂. Activator Pr³⁺ and crystals can include: LaF₃, LaCl₃, LaBr₃, PrCl₃, and PrBr₃. Activator Cr³⁺ and crystals can include: BeAl₂O₄, Al₂O₃, and Y₃Al₅O₁₂. Activator Eu³⁺ and crystals can include: Y₂O₃, YVO₄. Activator Gd³⁺ and crystals can include: Y₃Al₅O₁₂.

Some of the dopant-host combinations can also emit useful infrared light through excitation by absorption of a single photon. This invention can also include systems that emit infrared light by this process of down-conversion(e.g. absorbing a high energy photon and emitting one of lower energy) as well as systems that are excited by such two photon processes as up-conversion(e.g. absorbing more than one low energy photons and emitting one or more higher energy photons).

Unprecedented doping levels of the heavy metal luminophore can be achieved whilst maintaining even dispersion of the luminophore. The physical and mechanical properties of the polymer composite can be tailored by controlling the monomer and luminophore dopant composition.

The polymer host can be comprised of a copolymer of alkyl acrylate or alkyl methacrylate and a dialkyl vinylbenzylphosphonate, alkyl vinylbenzylphosphonic acid monoester, or vinylbenzylphosphonic acid, as shown in Fig. 1. The ratios of the acrylate or methacrylate to the phosphonate can range from approximately 95:5 molar ratio to approximately 20:80 molar ratio, respectively. Luminescent heavy metal ions such as rare earth compounds(for example, NaYF₄:ErYb) loading in the host polymer matrix can range from approximately 5 up to

approximately 80 weight percent. Stabilization of the dispersed heavy element luminophores can be accomplished through complexation with the phosphoryl moieties, as shown in Fig.1.

As described in the parent U.S. Patent applications previously cited, one can prepare the crystals as approximately 10 μm size particles and disperse them in a phosphorylated

5 polymethylmethacrylate (p-PMMA) host. This results in a display medium that can be formed to any desired shape, can be transparent or not, as desired, and can be affixed to any desired substrate. Experiments have been conducted using several different rare earth ions co-doped with Yb^{3+} in fluoride and orthophosphate crystalline hosts. The Yb^{3+} ions absorb light in a fairly broad band near approximately 975 nm in these crystals. They then can efficiently transfer the absorbed energy to levels of the co-dopant from which visible light can be emitted. This process, one in which sequential absorption of two photons of near infrared energy by donor ions which then transfer that energy to a single acceptor ion in such a manner as the acceptor can then emit visible light, is called up conversion.

10 An additional application of these composite materials can include their use as plastic optical fiber amplifiers, and the like.

15 While the invention has been described, disclosed, illustrated and shown in various terms of certain embodiments or modifications which it has presumed in practice, the scope of the invention is not intended to be, nor should it be deemed to be, limited thereby and such other modifications or embodiments as may be suggested by the teachings herein are particularly reserved especially as they fall within the breadth and scope of the claims here appended.

20